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IMPROVED ACID COPPER ELECTROPLATING SOLUTIONS

This application claims priority from Provisional Patent Application Number 60/144,159 filed July 15, 1999.

FIELD OF THE INVENTION

The present invention is related to an improved acid copper electroplating composition. More particularly, the present invention relates to the use of new carriers, brighteners and levelers as well as molecules that combine carrier/brightener and carrier/leveler functionality.

BACKGROUND OF THE INVENTION

Copper electroplating bath solutions are used in a variety of industries. In the semiconductor industry, there is an increasing need for these baths to meet decreasing device feature size, increasing wafer size and high yield. Various proprietary electroplating bath chemistries are commercially available that claim success with regards to the copper metallization process. Ideally, the bath chemistry should help to fill with copper small yet high aspect ratio trenches and vias, *e.g.* < 0.18 µm and aspect ratio > 5, to obtain uniform and void free plating while maintaining high production rates. The plating bath chemistries should also be relatively chemically stable, less corrosive and easily monitored and replenished.

Copper sulfate and sulfuric acid are the basics of the acid copper electroplating bath chemistry. Organic additives such as carriers, brighteners, levelers and combinations of these can offer a plating bath to fill the small and high aspect ratio

trenches and vias without voids or seams. As-plated copper deposits are of uniform thickness and fine grain size, and highly <1 1 1> crystal orientated.

Carriers typically are water-soluble polymers containing -$(CH_2)_n$-O- where n = 1 to 3 or branched derivatives in the main chains. Carriers can form a monolayer film at the cathode surface, which is a barrier to the diffusion of Cu^{+2} ions to the surface and polarizes the cathode. The proper polarization of the cathode is a prerequisite for producing fine and orientated grain structure. However, carriers tend to decompose into lower molecular fragments at both the cathode and the anode, and lose polarization effectiveness. As such, carriers with high stability are desired.

Brighteners not only produce fine and orientated grain structure for the as-plated deposits but also provide better chemical stability and solubility in the electroplating bath. Brighteners are typically water-soluble sulfonic acids containing mercapto and/or thio groups. U. S. Pat. No. 5,151,170 teaches a brightener that consists essentially of the hydrogen peroxide oxidation product of a dialkylamino-thioxomethyl-thioalkanesulfonic acid wherein each alkyl and alkane group individually contains 1 to 6 carbon atoms. They can produce fine copper deposits by masking the preferential growth sites/planes. Current brighteners can suffer from poor stability, oxidation by air and electrochemical oxidation at the anode, as well as catalytic decomposition at the copper surface. The decomposed products are often detrimental to copper deposition properties.

Levelers play a key role in void and seam free trench filling, *i.e.*, superfilling or bottom-up filling. The deposition rate needs to be much faster at the bottom of the features than on the side wall and shoulder of the trenches and vias. As such, different molecular size levelers are employed to tailor different generation (or size) of trenches and vias. The large molecular size is usually preferred for the filling of larger trenches and vias since the diffusion of the levelers towards the bottom of trenches is much slower, which in turn, results in extremely low leveler flux at the bottom and promotes bottom-up filling or superfilling. However, the larger molecular size can eventually block the openings and prevent the copper ions from entering the trenches.

This consequently creates voids when the size of the trench and vias is greatly reduced (*e.g.*, ~0.1 μm).

Various chemically combined brightener/carrier and/or leveler/carrier can further enhance these functions and goals. The as-plated copper deposits can complete self-annealing process in several hours to have a stable microstructure at room temperature.

DESCRIPTION OF THE RELATED ART

U.S. Pat. No. 5,051,154 teaches an aqueous electroplating solution comprising at least one soluble copper salt, an electrolyte and at least one organic additive capable of modifying the charge transfer overpotential of the solution in an amount sufficient to shift the overpotential by at least 150 millivolts and being independent of solution agitation. This reference teaches using a wetting agent as a component additive in the system capable of modifying the charge transfer overpotential. Additional additives can include a brightener along with the wetting agent and this can be selected from the group consisting of *n,n*-dimethyl-dithiocarbamic acid - (3-sulfopropyl) ester; 3-mercapto-propylsulfonic acid(sodium salt); carbonic acid-dithio-*o*-ethylester-s-ester with 3-mercapto-1-propane sulfonic acid(potassium salt); bisulfopropyl disulfide; 3-(benzthiazolyl-*s*-thio) propyl sulfonic acid (sodium salt); and pyridinium propyl sulfobetaine. The three component additive may also include levelers such as those selected from the group including 1-(2-hydroxyethyl)-2-imidazolidinethione; 4-mercaptopyridine; 2-mercaptothiazoline; ethylene thiourea; thiourea; and alkylated polyalkyleneimine.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides for an improved acid copper electroplating bath composition and method for preparing them. The composition comprises an aqueous solution of acid and copper salt, and the improvement comprises the addition of at least one of a carrier; a water soluble mercapto-containing organic brightener

compound; and a leveler which comprises an organic compound containing single or multiply charged centers in acidic bath solution.

In addition the present invention provides for a method for copper plating or metallization of advanced interconnects (less than 0.18 microns and having an AR (Aspect Ratio) greater than 6) comprising immersing a substrate intended for advanced interconnects into the copper electroplating composition and conducting an electrochemical deposition process.

In a typical acid copper electroplating bath, an acid and copper salt are employed. The acid is typically sulfuric acid while the copper salt can be selected from the group consisting of copper sulfate, copper acetate, copper fluoborate, cupric nitrate and copper pyrophosphate. Additional inorganic additives can include both chloride and alkaline species. The chloride can enhance cathode surface adsorption of organic additives such as the carrier and improve the oxidation of the anodes to improve plating efficiency. Alkaline species such as ammonium hydroxide are added to reduce the acidity and corrosivity of this bath solution. Chloride is added in an amount of about 20 to 100 parts per million parts water in the bath, while the alkaline is added in an amount necessary to reduce the solution's pH.

For the purposes of the present invention, the acid copper electroplating solution will have from about 50 to about 250 grams of copper salt per liter of water and about 60 to about 250 grams of sulfuric acid per liter of water.

In addition to sulfuric acid, copper salt, and inorganic additives disclosed above, as is known in the art, one or more of organic additives such as carriers, brighteners, levelers, and combinations of these are also employed to obtain high throwing power to fill the small and high aspect ratio trenches and vias.

The carriers used in this invention can comprise conventional ones in the art, *e.g.*, polyethylene glycol and poly(ethylene oxide), and a new class of carriers - polysaccharides. The polysaccharides consist of simple sugars such as fructose and

glucose linked by glycosidic bonds. Representative examples include but are not limited to starch, cellulose, amylopectin and amylose.

The brighteners useful in this invention possess both stability and solubility in the copper electroplating bath. The brighteners include both water soluble mercapto-containing organic compounds and other organic sulfides. Representative examples include but are not limited to *N*-methylallyl-*N'*-methylthiourea; tetramethylthiuram disulfide; ethylethylthiomethyl sulfoxide; ammonium diethyldithiocarbamate; dimethyl-2-thioxo-1,3-dithiole-4,5-dicarboxylate; 3-mercapto-1-propanesulfonic acid sodium salt; 3-mercapto-1-propanesulfonic acid; bis (2-mercaptoethyl) sulfide; ethylene trithio carbonate; ethanethiol; 2-mercaptoethanol; monothioglycerol (1-thioglycerol); 1,2-ethanedithiol; and thiodiethanol. The most preferred brighteners are ammonium diethyldithiocarbamate, 3-mercapto-1-propanesulfonic acid sodium salt, and its free acid form. 3-Mercapto-1-propanesulfonic acid is prepared from 3-mercapto-1-propanesulfonic acid sodium salt by an ion-exchange process using cation ion-exchange resins such as Dowex DR2030 (20-30 mesh), Dowex HCR-W2 (16-40 mesh), Dowex 50Wx8-100 (50-100 mesh, 1.7 meq / mL, 0.80 g / mL), and Dowex 50Wx8-200 (100-200 mesh, 1.7 meq / mL, 0.80 g / mL). The sodium level can be reduced to a few ppm from ~1500 ppm in original 1 wt.% aqueous solution. Both a packed column with ion-exchange resin and a reaction flask approach using ion-exchange resin can remove sodium to low ppm levels.

The need for a sodium-free brightener is important in avoiding sodium contamination of the copper deposited thin layer. The 3-mercapto-1-propanesulfonic acid was prepared by both ion-exchange column and in a reaction flask, and sodium removal efficiency was better than 99% for both methods. This is important regarding bath life as the buildup of sodium in the bath over time would require the bath to be dumped and replenished once the sodium level becomes unacceptably high.

The levelers useful in this invention possess single or multiple positively charged centers that will form single or multiple positively charged sites after protonation in the acidic conditions of the bath. In this invention, the levelers are divided into three groups - polymeric levelers, low molecular weight

levelers, and organic dyes. Representative examples of polymeric levelers include but are not limited to polyethylenimine, 80% ethoxylated; poly(allylamine); poly(allylamine hydrochloride); polyaniline, sulfonated, 5 wt. % in water, 75 mole % sulfonated; poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, quaternited; poly[*N,N'*-bis(2,2,6,6-tetramethyl-4-piperidinyl)-1,6-hexanediamine-*co*-2,4-dichloro-6-morpholino-1,3,5-triazine; polyacrylamide; poly(acrylamide-*co*-diallyldimethylammonium chloride); poly(diallyldimethylammonium chloride); poly(melamine-*co*-formaldehyde), partially methylated; poly(4-vinylpyridine), 25% cross-linked; poly(1,2-dihydro-2,2,4-trimethylquinoline). The most preferred polymeric levelers are poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, quaternited, and poly(diallyldimethylammonium chloride).

Representative examples of low molecular weight levelers include but are not limited to *N*-containing acyclic systems, *N*-containing five-membered heterocyclic systems, and *N*-containing six-membered heterocyclic systems. Most of them also contains mercapto-, sulfide, or disulfide functionalities. Representative examples of *N*-containing acyclic systems include 2,5-dithiobiurea, dithiooxamide, 1-phenyl-2-thiourea, and diethylenetriamine. The most preferred one is diethylenetriamine. Representative examples of *N*-containing five/six-membered heterocyclic systems include *p*-xylenebis(tetrahydrothiophenium) chloride, 2-thiohydantoin, pseudo thiohydantoin, (R)-(-)-thiazolidine-4-carboxylic acid, 3-(2'-thiopyridinium) propyl sulfonate, 2,2'-dipyridyl disulfide, 4,4'-dipyridyl disulfide, thionicotinamide, 4-(trifluoromethyl) -2-pyrimidinethiol, 2-mercapto-4-methylpyrimidine hydrochloride, 5-phenyl-1 *H*-1,2,4-triazole-3-thiol, 5-(4'-pyridyl)-1 *H*-1,2,4-triazole-3-thiol, 2-amino-6-purinethiol, 4-amino-5-(4'-pyridyl)-4 H-1,2,4-triazole-3-thiol, diethyl heptadedecyl imidazolinium ethylsulfate, hexamethylenetetraamine, 1,3-bis(3-pyridylmethyl)-2-thiourea, 2,4-diamino-6-mercaptopyrimidine hemisulfate, dithiouracil, 4,5-diamino-2,6-dimercaptopyrimidine, 4,5-diamino-6-hydroxy-2-mercaptopyrimidine hemisulfate hydrate, 4(5)-imidazoledithio-carboxylic acid, 2-mercapto-5-benzimidazolesulfonic acid, sodium salt dihydrate, 2-thiouracil, trithio cyanuric acid, (2-pyrimidylthio) acetic acid, 7-trifluoromethyl-4-quinlinethiol, 5-carbethoxy-2-thiouracil, 1 *H*-1,2,4-triazole-3-thiol, 1-phenyl-1 *H*-1,2,4-triazole-5-

thiol, *N,N'*-ethylene-thiourea, and 2-mercapto benzothiazole. The most preferred one is thionicotinamide.

Representative examples of organic dyes include but are not limited to Bismarck Brown Y, Chicago Sky Blue 6B, and Acid Violet.

The organic additives are constantly consumed due to breakdown and oxidation in the electroplating process. The consumed additives are generally compensated for by a replenishing process to maintain constant bath chemistry. Numerous consumption/replenishment cycles may proceed before a complete replacement of the plating bath is necessary. As a result of this process, there is an accumulation of contaminants which can be a critical problem. The contaminants may interfere with the functioning of organic additives and may cause inconsistent plating that is unacceptable to the semiconductor industry.

It has been found that removal of organic additives can be accomplished with activated carbon such as type 4040 and DCL activated carbon from Barneby Scientific Corp. The bath can be filtered through an activated carbon bed and returned to the plating bath without the need for dumping and restocking the plating bath. The increased number of cycles without having to remake the bath improve effectiveness and economics of the plating process.

This consumption and breakdown of the plating bath additives will result in the need for replenishment of these additives. An accurate determination is needed in-situ and feedback provided fairly rapidly to enable efficient use of baths by semiconductor fabs. The criteria for this analysis include the ability to separate bath components, minimum detection limits, measurement time, accuracy and repeatability and the complexity and frequency of calibration and maintenance. Electrochemical analytical techniques such as cyclic voltammetric stripping (CVS), AC-cyclic voltammetry (AC-CV), AC impedance spectroscopy (AC-IS) and pulsed cyclic galvanostatic analysis (PCGA) have been employed. CVS is generally preferred as it provides relatively high measurement accuracy and fast test results while not generating waste. High performance liquid chromatography (HPLC) is also employed

as it offers the advantage of allowing quantitative measurement of contaminants and determination of break-down additives.

The invention further comprises the use of molecules that combine brightener/carrier and carrier/leveler functionalities. The combination of brightener/carrier is typically a monomeric to polymeric protein chain where the chain is linked by sulfide and disulfide bridges. The combination of carrier/leveler can help improve the stability of the leveler while simplifying the bath by reducing the number of organic additives. Such materials can be poly[bis(2-chloroethyl)ether-*alt*-1,3-bis[3-(dimethylamino)propyl]urea, quaternited, and poly(melamine-*co*-formaldehyde), partially methylated.

The carrier of the present invention may be added in an amount ranging from about 2 to about 1000 parts per million parts water. The leveler may be added in an amount of about 2 parts to about 1000 parts per million parts of water in the electroplating solution.

The brightener may be added in an amount ranging from about 5 parts to about 100 parts per million parts water. When the combination carrier/brightener is employed, it is added in an amount ranging from about 5 to about 100 parts per million parts water. The combination carrier/leveler when employed may be added in an amount ranging from about 2 to about 1000 parts per million.

Other additives that are found in the baths include wetting agents such as carboxylic acids and antioxidants. Carboxylic acids such as citric acid improve wetting ability of the cathode and provide better adsorption of the organic additives to the cathode. Typically, these are added in a range of about 2 to about 1000 parts per million parts water in the bath.

Brighteners tend to be oxidized in the vicinity of the anode during and without plating. Oxidized brighteners lose their functionality and cause an inconsistent plating rate and poor quality of the as-plated object. The oxidizing agents near the cathode are typically hydrogen peroxide and oxygen. The present inventors have

discovered that continuously purging the bath solution near the anode side with an inert gas will expel oxygen out of the solution.

The additive packages of the present invention may be added to the aqueous acid copper electroplating bath either individually or as combinations depending upon the type of substrate being plated.

The plating solutions of this invention are used in a conventional manner. They are preferably used at room temperature or higher temperature. During plating, the bath solution is preferably agitated by inert gas, air sparger or by mechanical means. The plating current density can range between 3 mA/cm^2 and 40 mA/cm^2 depending on aspect ratio of trenches and vias. The wave form can be direct current (DC), pulse current (PC) or pulse reverse current (PRC).

In studies performed using 67 g/l of $CuSO_4$-$5H_2O$, 170 g/l of H_2SO_4 and 45 g/l of Cl^- as the starting bath, good plating results were obtained using a current density of 3.2 mA/cm^2 and 25.5 mA/cm^2 with DC, PC or PRC wave form. The following additive combinations produced the best results regarding trench filling.

Plating Solution	Composition (PPM)
1	C1(20) B1(12) L1 (15)
2	C1(20) B1(12) L2 (25)
3	C1(20) B1(12) L3 (25)
4	C1(20) B1(12) L4 (25)

C1 is polyethylene glycol
B1 is 3-mercapto-1-propanesulfonic acid sodium salt
L1 is poly(diallyldimethylammonium chloride)
L2 is diethylenetriamine
L3 is (R)-(-)-thiazoline-4-carboxylic acid
L4 is poly[bis(2-chloroethyl)ether-alt-1,3-bis[3-(dimethyl amino)propyl]urea, quaternited, 62 wt. % in water.

While this invention has been described with respect to particular embodiments thereof, it is apparent that numerous other forms and modifications of this invention will be obvious to those skilled in the art. The appended claims and this invention generally should be construed to cover all such obvious forms and modifications which are within the true spirit and scope of the present invention.